OFFICE OF NAVAL RESEARCH

END-OF-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

R&T code 313r001

Contract No. N0014-89-J-1746

Ultrafast Near-Field Scanning Optical Microscopy (NSOM) of Emerging Display Technology Media: Solid State Electronic Structure and Dynamics

Paul F. Barbara

Department of Chemistry

University of Minnesota

Minneapolis, MN 55455

May 31, 1995

Female Graduate Students: __0__
Female Post-Doctoral Associates: __0__
the number of
Minority* Graduate Students: __0__
Minority* Post-Doctoral Associates: __0__
and, the number of
Asian Graduate Students: __0__
Asian Post-Doctoral Associates: __0__

l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

+ Use the letter and an appropriate title as a heading for your list, e.g.:
b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via email or via PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

a. Submitted Paper to Refereed Journals

1. **"Molecular Structure and Exciton Dynamics in J-Aggregates by Polarization-Dependent Imaging with Near Field Scanning Optical Microscopy"**, D.A. Higgins, P.J. Reid, and P.F. Barbara, J. Phys. Chem., submitted.

b. Published Papers

1. **"Evidence for Intermolecular Hydrogen-Bond Rearrangement in the Electron Transfer Dynamics of Betaine-30 in n-Butanol"**, P.J. Reid, S. Alex, W. Jarzeba, R.E. Schlief, A.E. Johnson, and P.F. Barbara, Chem. Phys. Lett., 229, 93 (1994).

2. **"Excitonic Transitions in J-Aggregates Probed by Near-Field Scanning Optical Microscopy"**, D.A. Higgins and P.F. Barbara, J. Phys. Chem., 99, 3 (1995).

c. None

d. None

e. None

f. None

g. None

h. Invited Conferences
(major expenses paid by conference)

Radiation Chemistry Gordon Conference, Salve Regina University, RI, July 17-22, 1994

208th ACS National Meeting, Washington, DC, August 21-26, 1994

"Electron Transfer in Photosynthesis" workshop, University of Jyväskylä, Finland, December 15-18, 1994

Australian Conference on Physical Chemistry, Canberra, Australia, February 12-16, 1995

NAIR Cluster Science Workshop, Ibaraki, Japan, March 3-7, 1995

APS National Meeting, San Jose, CA, March 22-24, 1995

"Scanning '95", Monterey, CA, March 29-30, 1995

209th ACS National Meeting, Anaheim, CA, April 2-7, 1995

i. Submitted Conferences

208th ACS National Meeting, Washington, DC, August 21-26, 1994

FACSS Meeting, St. Louis, MO, October 1-6, 1994

j. Honors/Awards/Prizes

Appointed 3M Distinguished Research Professor

Heinlein Hall Lecture, Bowling Green State University, 1994

William Draper Harkins Lecture, University of Chicago, 1995

McElvain Seminar Series, University of Wisconsin, 1995

Member Advisory Board, Journal of Physical Chemistry, 1990-93, 1994-97.

Member Advisory Board, Journal of the American Chemical Society, 1995-98.

Member Advisory Board, Accounts of Chemical Research, 1994-95.

Member Advisory Board, Molecular Physics, 1994-97.

Member Advisory Board, Review of Scientific Instruments, 1994-97.

Member Advisory Board, Journal of Chemical Physics, 1994-97.

Member Advisory Board, Chemical Physics, 1994-present

Executive Committee, Interamerican Photochemical Society, 1992-96.

Chair, Division of Physical Chemistry, ACS

k. Graduate Students

Joseph Kerimo
Andre Kosterin

Postdoctoral Associates

Dan Higgins (supported by Fellowship)
David vanden Bout (supported by Fellowship)
Phil Reid

l. Other Funding

NSF, "Ultrafast Measurements on Theoretically Tractable Prototypes for Polar Solution Chemistry", June 1, 1993 - November 30, 1996, $352,000.

DOE, "Femtosecond Time-Resolved Experiments on the Solvated Electron and Intermolecular Charge Transfer Solution", May 1, 1995 - April 30, 1998, $455,000.

PART II

a. Principal Investigator: Paul F. Barbara
b. Telephone Number: 612-625-0064
c. Cognizant ONR Officer: John Pazik

d. Description of Project

The main focus of our project is the further development and application of NSOM to studies of the local photophysical and photochemical properties of complex nanostructured materials. We are directly involved in the currently-rapid advance of NSOM methodologies and are especially interested in ultrafast time-resolved applications of NSOM. Our ultrafast NSOM currently allows for picosecond (and in the near future, femtosecond) time resolution to be obtained with nanometer-scale spatial resolution. In our experiments we are addressing questions pertaining to variations in excited state lifetimes, charge and energy transfer rates, and charge and energy transfer distances and directionality in highly nanostructured materials. These results are being employed along with static imaging and polarization-dependent imaging, as well as static spectroscopic measurements, to provide invaluable information on how nanoscale structural variations lead to variations in the important local photophysical and photochemical properties of numerous technologically-important, nanostructured samples.

e. Significant Results in the Last Year

In the past year we have upgraded our existing NSOM instrumentation and have begun development of a new NSOM instrument in direct collaboration with Topometrix (the provider of our commercial NSOM). The existing NSOM was modified to make a broader spectral range available for fluorescence microscopy/spectroscopy and a new ultrafast detector and electronics were added to allow for picosecond measurements of fluorescence lifetimes with nanometer-scale spatial resolution. We have obtained high resolution fluorescence images and local fluorescence spectra of nanometer-scale regions in J-aggregate films with the NSOM instrument. These results are the highest resolution optical images of aggregates obtained to date and demonstrate that the J-aggregate films are highly nanostructured but possess a well-ordered internal molecular structure. Polarization-dependent imaging was used to determine the orientation of the molecules in the aggregate; a structural model was developed based on these results. Finally, picosecond time-resolved measurements of the excited state lifetimes in aggregates were made with the ultrafast NSOM apparatus to obtain valuable information on the mechanisms for excited state decay in nanoscale aggregate structures. We have also been

developing "standard samples" for NSOM and have achieved single molecule detection with our NSOM. Our experimental results and instrumental developments have made invaluable contributions to Topometrix and to the demonstration of the Topometrix Aurora instrument as a state-of-the-art NSOM apparatus. We have been in direct contact with scientists at Topometrix throughout this project and have visited Topometrix on several occasions.

f. Plans for Future Work

Future work in our lab will involve further development of NSOM technology and new applications of NSOM to studies of technologically-important nanostructured materials. A new NSOM is currently being developed in our laboratory in direct collaboration with Topometrix. This new NSOM will incorporate a closed-loop position feedback system that will allow for more accurate location and investigation of nanoscale features in our samples. In addition, construction of an ultrafast NSOM instrument with femtosecond time resolution based on pump-probe methodologies is currently underway and will incorporate an existing femtosecond Ti:sapphire laser system. The new and existing NSOM systems in our lab will be directly employed in future studies of J-aggregate films, which find widespread application in photographic film, as well as in numerous other samples. Future samples we will study include photoluminescent and electroluminescent porous silicon which has applications in new detector and display technologies, and also polymer-based light-emitting diodes. Other samples will include dye-doped polymer and copolymer systems and rare-earth-doped IR-visible upconversion phosphors. Static and time-resolved NSOM studies of these samples promise to provide valuable new information on how nanoscale structural variations effect local photophysical and photochemical properties in these nanostructured systems.

g. Graduate Students and Postdoctoral Fellows Working On The Project

Graduate Students
Joseph Kerimo
Andre Kosterin

Postdoctoral Fellows
Dan Higgins (supported by Fellowship)
David Vanden Bout (supported by Fellowship)
Phil Reid

Ultrafast Near-Field Scanning Optical Microscopy (NSOM) of Emerging Display Technology Media: Solid State Electronic Structure and Dynamics

Prof. Paul F. Barbara
Dept. of Chemistry
University of Minnesota

APPROACH THIS PAST YEAR:

Static Imaging and Picosecond Time-Resolved Lifetime Measurements of Fluorescence from J-Aggregates with NSOM

FUTURE APPROACH:

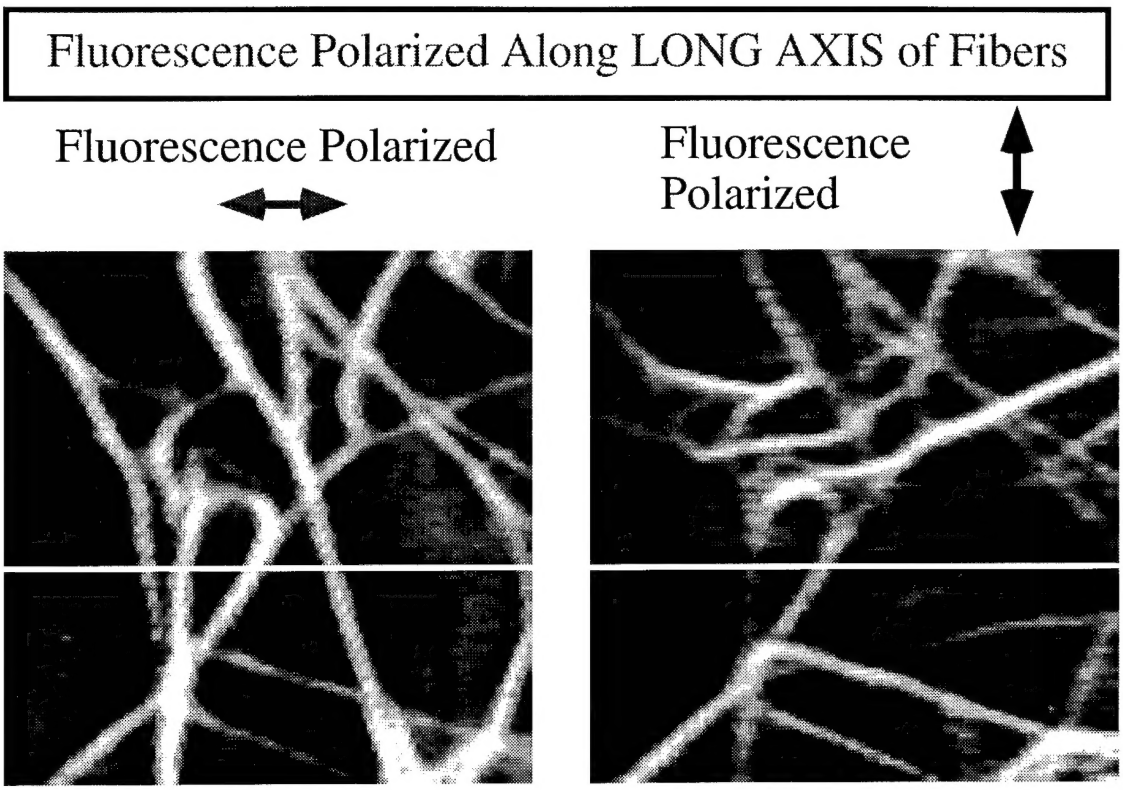
Femtosecond Pump-Probe NSOM of J-Aggregates and Other Solid State and Molecular Materials Important to Display Technology

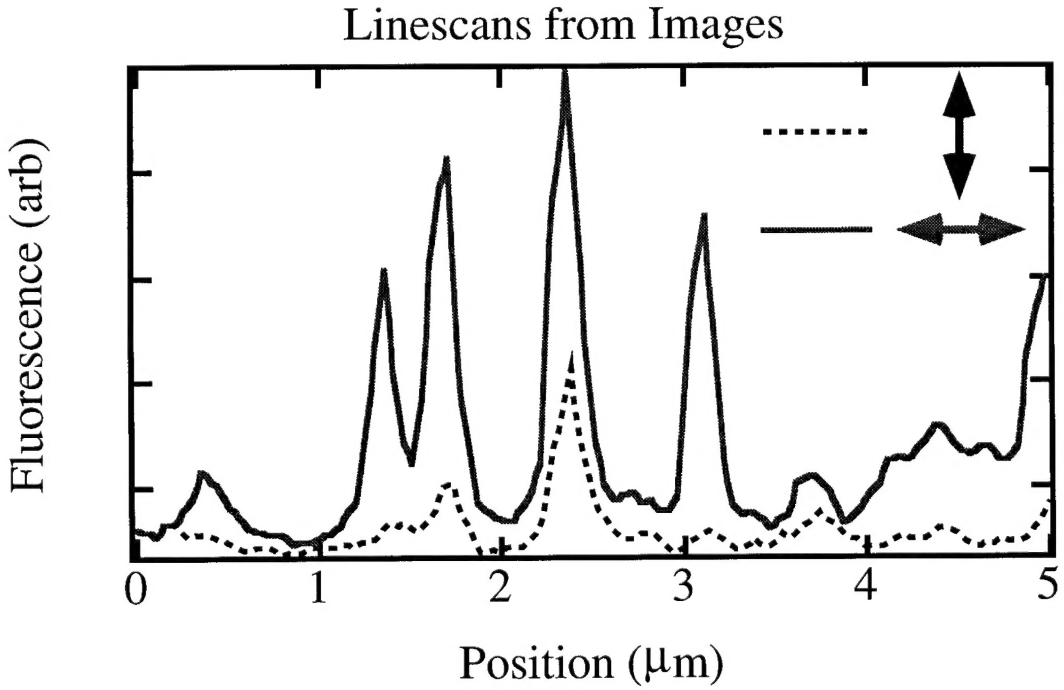
ULTIMATE GOAL:

FEMTOSECOND TIME RESOLUTION
AND
NANOSECOND SPATIAL RESOLUTION

Polarization-Dependent Fluorescence NSOM Images of J-Aggregate Films

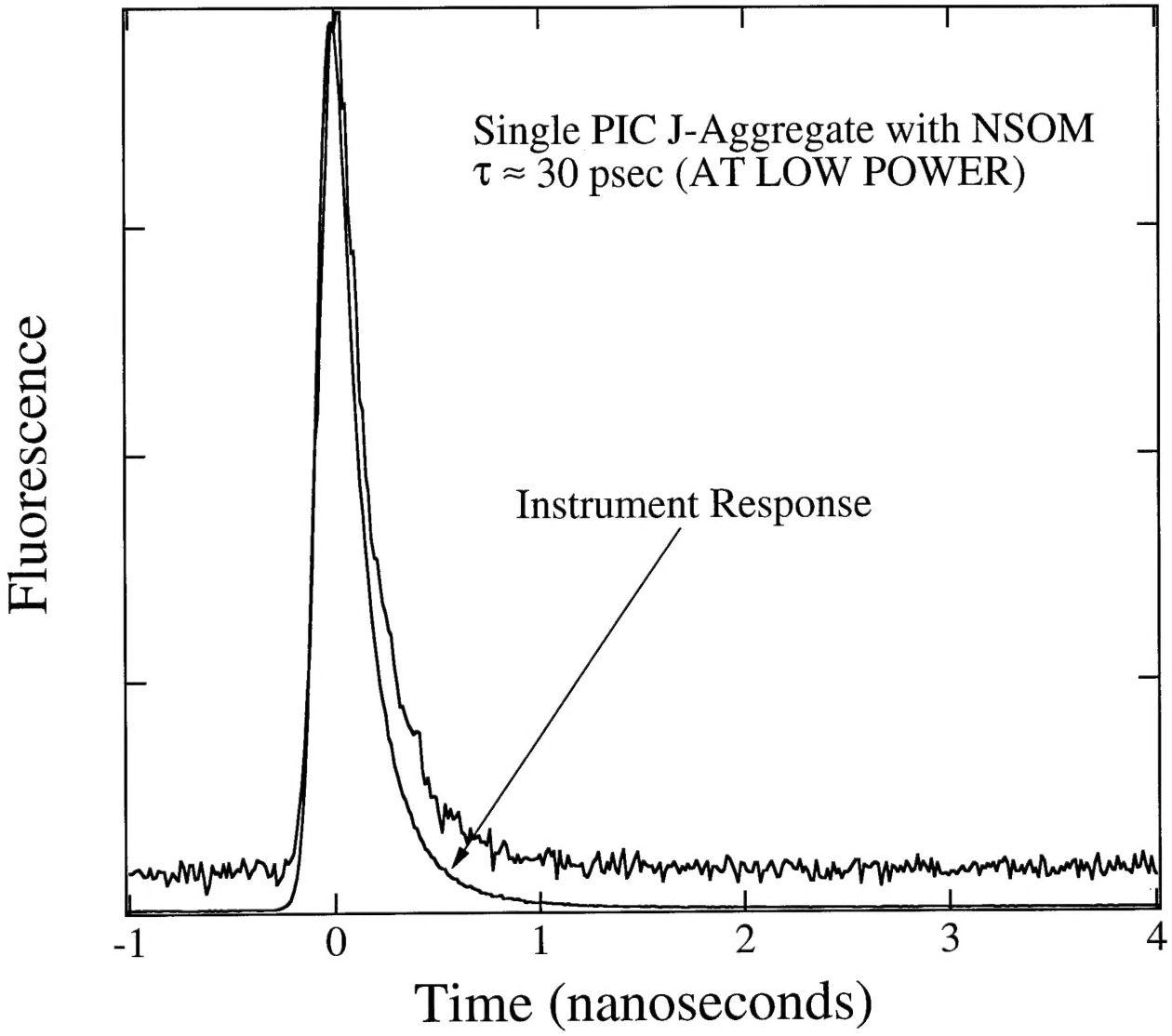
Fluorescence Detected at 575 nm





Single J-Aggregate Lifetimes with NSOM and Time Correlated Single Photon Counting

Simultaneous Picosecond Time Resolution/ Nanometer Spatial Resolution



Bulk Lifetime Measurement Yielded $\tau = 40$ psec

($\tau \approx 25$ psec at high power)

Ultrafast NSOM and New Display Technology

Prof. Paul F. Barbara

Past Results:

- Demonstration of Sensitivity of Topometrix NSOM - Imaging of Single Molecules
- Highest Resolution Optical Images of Nanostructured J-Aggregate Films
- Internal Molecular Structure and Long-Range Order in Aggregates by Polarization-Dependent NSOM
- Distance Scale for Energy Migration in Aggregates by Spatial Photobleaching
- First Nanoscale Measurements of Excited State Lifetimes in Aggregates by Time Resolved NSOM

Future:

- Femtosecond Experiments on Important New Samples:

  Porous Silicon, Polymer-Based Light-Emitting Diodes, Rare-Earth-Doped Upconversion Phosphors, Dye Crystal Systems

EXPLANATORY TEXT

Near-field scanning optical microscopy (NSOM) is a newly-developed form of microscopy which allows for visible-light imaging of materials with spatial resolution much better than can be obtained with any other form of optical microscopy. In addition to high resolution imaging, since NSOM uses light as the imaging mechanism, numerous previously-developed spectroscopic techniques can be coupled with NSOM and can be used to study nanostructured materials without the "averaging" effects that are problematic in studies of complex materials with bulk spectroscopic techniques. The main focus of our project is the further development and application of NSOM to studies of the local photophysical and photochemical properties of complex nanostructured materials important to emerging display technologies. We are directly involved in the rapidly advancing field of NSOM and are especially interested in ultrafast time-resolved applications of NSOM. Our ultrafast NSOM currently allows for picosecond time resolution to be obtained with nanometer-scale spatial resolution and we are actively pursuing the implementation of femtosecond pump-probe techniques in our NSOM. The scientific questions we seek to address involve the effects of the local physical properties of nanostructured materials on their observed photophysical and photochemical properties and how these variations may effect the properties of image display devices constructed from such nanostructured materials. Through static and time-resolved NSOM experiments on nanostructured J-Aggregate films we are currently studying such subjects as film structure, internal molecular structure, excited state lifetimes, energy transfer rates, and energy transfer distances and directionality. These results are being employed to provide invaluable information on how nanoscale structural variations lead to variations in the important local photophysical and photochemical properties of J-aggregates and similar materials. J-Aggregates provide highly nanostructured films for basic studies of these types of effects and also find widespread use as sensitizers in photographic film, therefore the understanding of the effects of nanostructures on their local properties is of utmost importance. Future work in our lab will involve further development of NSOM technology and new applications of NSOM to studies of other technologically-important nanostructured materials. New and existing NSOM systems in our lab will be directly employed in future studies of J-aggregate films and numerous other samples which include photoluminescent and electroluminescent porous silicon, which has applications in new detector and display technologies, and also polymer-based light-emitting diodes. Other samples will include dye-doped polymer and copolymer systems and rare-earth-doped IR-visible upconversion phosphors, the latter having applications in 3-D display technology. Static and time-resolved NSOM studies of these samples promise to provide new information on how nanoscale structural variations effect local photophysical and photochemical properties in these systems.